

Magnetic phase diagram of $\text{Sr}_{1-x}\text{Ca}_x\text{Co}_2\text{P}_2$

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Abstract. In order to study the phase diagram from a microscopic viewpoint, we have measured wTF- and ZF- μ^+ SR spectra for the $\text{Sr}_{1-x}\text{Ca}_x\text{Co}_2\text{P}_2$ powder samples with $x = 0, 0.2, 0.4, 0.5, 0.6, 0.8$, and 1. Due to a characteristic time window and spatial resolution of μ^+ SR, the obtained phase diagram was found to be rather different from that determined by magnetization measurements. That is, as x increases from 0, a Pauli-paramagnetic phase is observed even at the lowest T measured (1.8 K) until $x = 0.4$, then, a spin-glass like phase appears at $0.5 \leq x \leq 0.6$, and then, a phase with wide field distribution probably due to incommensurate AF order is detected for $x = 0.8$, and finally, a commensurate A -type AF ordered phase (for $x = 1$) is stabilized below $T_N \sim 80$ K. Such change is most likely reasonable and connected to the shrink of the c -axis length with x , which naturally enhances the magnetic interaction between the two adjacent Co planes.

1. Introduction

The appearance of unconventional superconductivity in iron pnictides with the ThCr_2Si_2 -type (122) structure, i.e. $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ reconfirmed the competition between antiferromagnetism and superconductivity [1, 2]. Similar to the K-doping effect, the magnetic state of CaFe_2As_2 varies with pressure from antiferromagnetic (AF) to superconducting, and finally to nonmagnetic [3], while its structure changes from an “uncollapsed tetragonal” (uc T) phase, an orthorhombic phase, and a “collapsed tetragonal” (c T) phase [4]. Here, in the collapsed phase, the ratio of stacking to in-plane lattice parameters (c/a) is significantly smaller than that expected from simple atomic size considerations [5].

In contrast to CaFe_2As_2 and BaFe_2As_2 , the related compounds, $AM_2\text{P}_2$ with $A = \text{Ca, Sr, and Ba}$, and $M = \text{Fe, Co, and Ni}$ do not show unconventional superconductivity, but exhibit an interesting magnetic transition with the structural change. For the present target system, $\text{Sr}_{1-x}\text{Ca}_x\text{Co}_2\text{P}_2$, the crystal structure changes from uc T for $x = 0$ to c T for $x = 1$ [6]. According to the electronic and magnetic phase diagram determined from the macroscopic

measurements [6], the system evolves from a nonmagnetic metallic ground state to an AF metallic ground state through a crossover composition regime at $x \sim 0.5$. Then, in the x range between 0.8 and 0.9, the system manifests a FM-like ground state within which the magnetic ordering temperature is highest at $x \sim 0.9$. For the sample with $x \geq 0.9$, an AF ground state reappears [7]. A similar behavior was also reported for $\text{Ca}(\text{Fe}_{1-x}\text{Co}_x)_2\text{P}_2$ [8], $\text{Ca}(\text{Ni}_{1-x}\text{Co}_x)_2\text{P}_2$ [8], and $\text{SrCo}_2(\text{Ge}_{1-x}\text{P}_x)_2$ [9].

Note that χ measurements usually give us a significant insight into the ground state of magnetically ordered solids. However, such measurements are sometimes not suitable, particularly for the materials exhibiting order with a broad field distribution, *i.e.* when short-range order, random, nearly-random order, or incommensurate order appears in a material, due to the absence of periodic structure and/or the presence of rapid fluctuations. We have therefore performed a $\mu^+\text{SR}$ experiment on $\text{Sr}_{1-x}\text{Ca}_x\text{Co}_2\text{P}_2$ in order to investigate the variation of the magnetic nature with the Ca content (x).

2. Experimental

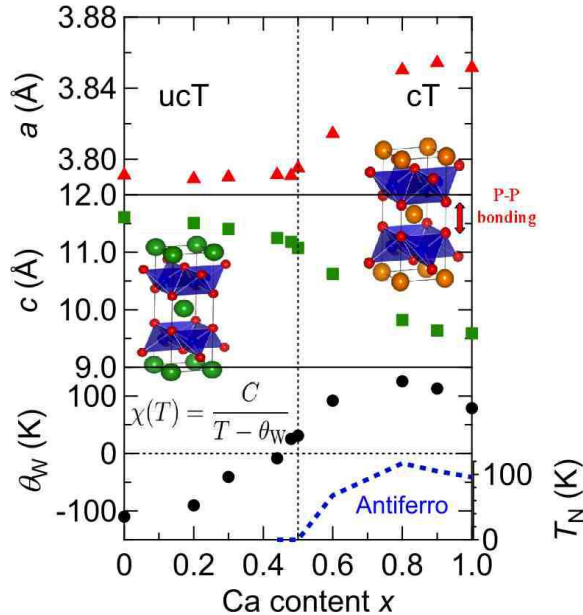


Figure 1. The change in the lattice constants and magnetic properties of $\text{Sr}_{1-x}\text{Ca}_x\text{Co}_2\text{P}_2$ with x determined by XRD analyses and χ measurements [11].

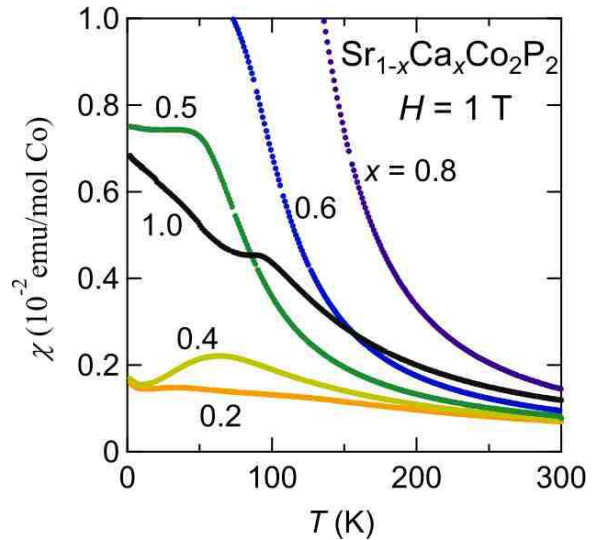


Figure 2. T dependence of χ for $\text{Sr}_{1-x}\text{Ca}_x\text{Co}_2\text{P}_2$ with $x \geq 0.2$ [11].

Polycrystalline samples of $\text{Sr}_{1-x}\text{Ca}_x\text{Co}_2\text{P}_2$ with $x = 0, 0.2, 0.4, 0.5, 0.6, 0.8$, and 1 were prepared from elemental P, Sr, Ca, and Co using two step reaction. For the first step, SrP, CaP, and Co_2P were synthesized by a solid state reaction between Sr (Ca, Co) and P in an evacuated quartz tube at 800°C (700°C for Co_2P). Then, for the second step, $\text{Sr}_{1-x}\text{Ca}_x\text{Co}_2\text{P}_2$ were synthesized by a solid state reaction between SrP, CaP and Co_2P at 1000°C for 20 hours in an Ar atmosphere. After grinding, the obtained powder was fired two times at 1000°C for 40 hours in an Ar atmosphere [10, 11].

According to powder x-ray diffraction (XRD) analyses, all the samples were single phase of tetragonal symmetry with space group $I4/mmm$. Also, as x increases from 0, the c -axis length monotonically decreases with x until ~ 0.5 , then rapidly decreases until 0.9, and finally,

levels off to a constant value above $x = 0.9$. This behavior is consistent with the literature [6]. Susceptibility (χ) measurements suggested the presence of magnetic transition above ~ 60 K for the samples with $x \geq 0.6$.

The μ^+ SR spectra were measured at surface muon beam lines using the **LAMPF** spectrometer of M20/TRIUMF in Canada. An approximately 500 mg powder sample was placed in an envelope with 1×1 cm² area, made with Al-coated Mylar tape with 0.05 mm thickness in order to minimize the signal from the envelope. Then, the envelope was attached to a low-back ground sample holder in a liquid-He flow-type cryostat for measurements in the T range between 1.8 and 150 K.

3. Results and discussion

Figure 3 shows the ZF- μ^+ SR spectrum for $\text{Sr}_{1-x}\text{Ca}_x\text{Co}_2\text{P}_2$ with $x = 0.5, 0.6, 0.8$, and 1 at the lowest T measured. The ZF-spectrum for CaCo_2P_2 exhibits a clear oscillation due to the formation of static AF order below $T_N \sim 80$ K, as reported by neutron diffraction measurements [7]. However, according to the detailed analysis, it was found that the ZF-spectrum consists of two muon-spin precession signals with different frequencies [$f_{\text{AF1}} = 34.6(1)$ MHz and $f_{\text{AF2}} = 9.5(3)$ MHz at 2 K]. As T increases from 2 K, the two signals disappeared at T_N . This suggests that there are two magnetically different muon sites in the CaCo_2P_2 lattice.

Although a clear oscillation is also observed in the ZF-spectrum for $\text{Sr}_{0.2}\text{Ca}_{0.8}\text{Co}_2\text{P}_2$, the initial phase (ϕ) was found to delay by $12 - 60^\circ$, when we attempted to fit the oscillatory signal by an exponential relaxing cosine function: $A_0 P_{\text{ZF}}(t) = A_{\text{AF}} \cos(2\pi f_{\text{AF}} t + \phi)$. This implies the wide distribution of an internal field at the muon site(s). The most probable reason is that the magnetic order is incommensurate (IC) to the lattice [12]. This is because, due to the mismatch of the period between the muon site(s) and magnetic order, IC order always provides an oscillatory signal with wide field distribution in the ZF- μ^+ SR spectrum. But, the other explanation is also available, as in the case for Ag_2NiO_2 [13] and LiCrO_2 [14]. Therefore,

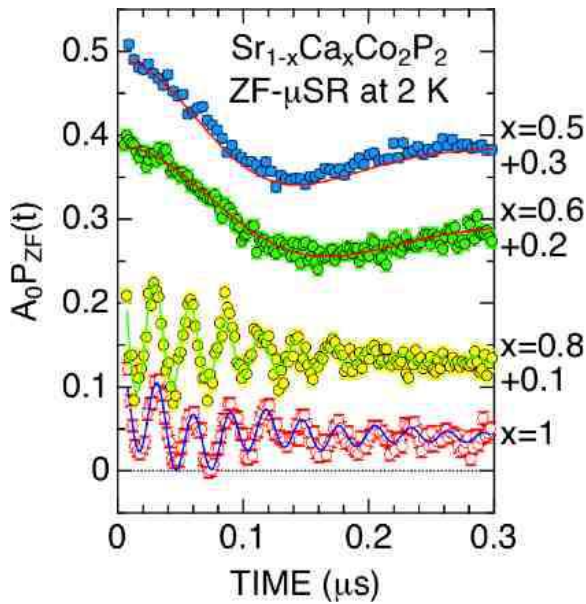


Figure 3. The ZF- μ^+ SR spectra at 2 K for the $\text{Sr}_{1-x}\text{Ca}_x\text{Co}_2\text{P}_2$ sample with $x = 0, 0.2, 0.4$, and 0.5 .

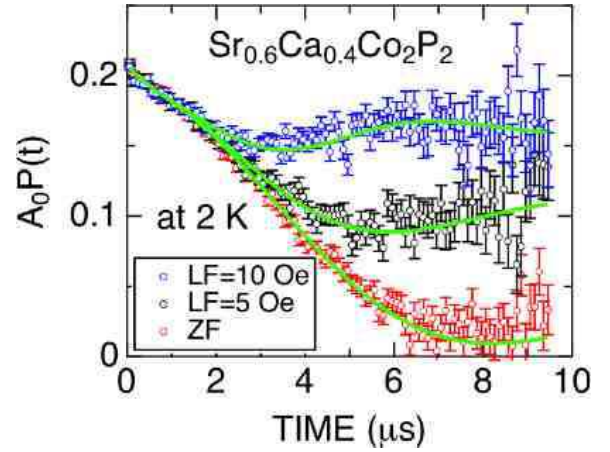


Figure 4. The ZF- and LF- μ^+ SR spectra at 2 K for the $\text{Sr}_{0.6}\text{Ca}_{0.4}\text{Co}_2\text{P}_2$ sample. The applied LF was 5 and 10 Oe. Solid lines represent the fit result using a static Gaussian Kubo-Toyabe function. By fitting both ZF- and LF-spectra using a common field distribution width (Δ), we can obtain reliable Δ .

neutron diffraction measurements is required for further clarifying the magnetic nature of the $x = 0.8$ sample.

For $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{Co}_2\text{P}_2$, the ZF-spectrum shows a static Kubo-Toyabe-type relaxation. Since the field distribution width (Δ) was estimated as $12 \times 10^6 \text{ s}^{-1}$ ($\sim 141 \text{ Oe}$), such KT behavior is naturally caused by disordered Co moments. Furthermore, weak transverse field $\mu^+\text{SR}$ measurements revealed the appearance of a large internal magnetic field below $\sim 50 \text{ K}$. Therefore, the ground state of $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{Co}_2\text{P}_2$ is most likely a spin-glass like state, although it is more preferable to measure AC- χ to confirm the spin-glass state. The situation for $\text{Sr}_{0.4}\text{Ca}_{0.6}\text{Co}_2\text{P}_2$ was the same to that for $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{Co}_2\text{P}_2$.

On the other hand, for the samples with $x \leq 0.4$, the ZF-spectrum exhibits an almost static KT behavior even at 2 K (Fig. 4), but $\Delta = 0.22 \times 10^6 \text{ s}^{-1}$ ($\sim 2.6 \text{ Oe}$). This is a typical value for nuclear magnetic fields at the muon site(s), and for this case, the origin is mainly due to the nuclear magnetic moment of ^{59}Co . Hence, the ground state for $\text{Sr}_{1-x}\text{Ca}_x\text{Co}_2\text{P}_2$ with $x \leq 0.4$ is assigned to be a Pauli-paramagnet.

Based on these results, the magnetic phase diagram for $\text{Sr}_{1-x}\text{Ca}_x\text{Co}_2\text{P}_2$ was determined (Fig. 5). That is, thanks to a unique power of $\mu^+\text{SR}$, the phase with $x \sim 0.8$ was found to be not an FM phase [6] but an incommensurate (IC) AFM phase. Then, next to the IC-AFM phase, a spin-glass (SG) like phase appears in the x range between ~ 0.7 and ~ 0.4 . The samples with $x \leq 0.4$ was found to be nonmagnetic down to 2 K . However, since the phase boundaries between C and IC, between IC and SG, and SG and PM are still not clarified, we need additional measurements on several $\text{Sr}_{1-x}\text{Ca}_x\text{Co}_2\text{P}_2$ samples.

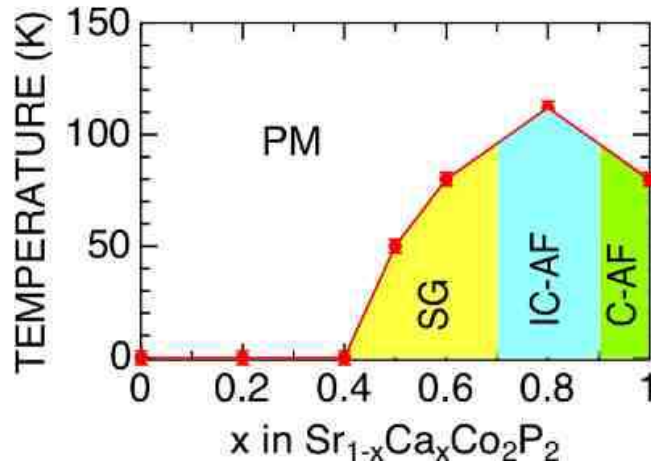


Figure 5. The tentative phase diagram for $\text{Sr}_{1-x}\text{Ca}_x\text{Co}_2\text{P}_2$ determined by $\mu^+\text{SR}$, where PM is a paramagnetic phase, SG is a spin-glass like phase, IC-AF is a phase with wide field distribution probably due to incommensurate AF order, and C-AF is a commensurate AF phase.

4. Acknowledgments

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